ALUMINATED LAYERED SILICATES AS PRECURSORS OF MESOPOROUS MOLECULAR SIEVES

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In 1993 a synthetic procedure describing preparation of the so-called folded sheet mesoporous materials (FSM) from the synthetic mineral kanemite (Inagaki et al., 1993) has been reported. Kanemite is a layered sodium silicate, with formula $NaHSi_2O_5 \cdot 3H_2O$, built of negatively charged tetrahedral silicon oxo-hydroxy zig-zag layers intercalated with positively charged octahedral layers of hydrated sodium cations, which are susceptible to cation exchange. Exchange of sodium cations for the cationic surfactant species results in the rearrangements within the silica layers and formation of structures with honey-comb appearance. Removal of the surfactant template by calcination produces porous materials of unique properties: hexagonal arrangement of uniform pores whose diameter can be controlled within 2–10 nm by changing the templating species, large specific surface area (over 700 m^2/g), and good thermal stability (up to 1100–1200°K).

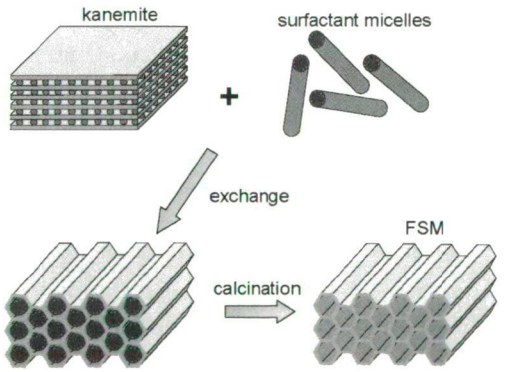

Fig. 1

Purely siliceous mesoporous materials do not contain active sites that would allow for their use as efficient adsorbents, molecular sieves, catalysts, etc. The aim of the present work was to obtain FSM materials substituted isomorphously with aluminium, in order to generate cation exchange properties in the FSM material. The first step of the preparation procedure involved the synthesis of a sodium silicate precursor, which, upon hydration transformed into kanemite. Alumination of the material has been carried out at this stage, by adding $Al(NO_3)_3$ to the synthesis mixture. The XRD patterns of the obtained solids pointed to the presence of several polymorphs of $Na_2Si_2O_5$, whose relative content depended on the amount of Al dopant. Subsequent hydration yielded solids which, beside XRD pattern characteristic of kanemite, showed also reflections assignable to a silicic acid $H_2Si_2O_5$ $7H_2O$. The contribution of the latter increased with the growing amount of Al substitution. A certain amount of amorphous silica, evidenced by a broad envelope centred around d = 0.35 nm, could be found in all solids. Upon treatment with the cationic surfactant (HDTMA, hexadecyltrimethylammonium chloride) and subsequent calcination all materials produced FSM-like structures as demonstrated by the characteristic XRD patterns typical of a hexagonal lattice. The observed d_{001} spacings depended on the Al content and were in the range 3.7–4.2 nm. Solid-state MAS NMR of ^{27}Al showed that in all samples Al occupied tetrahedral positions. Textural properties of the samples were determined from the nitrogen adsorption isotherm at 77°K. The BET specific surface areas were in the range 700–1000 m^2/g. The pore size distribution analysis with BJH method confirmed that all FSM materials were characterised by a uniform pore diameter, ranging from 2.4 nm for FSM without Al and with 2.5at% Al, to 2.8 nm for FSM with 5% Al.

Acknowledgements

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Reference

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